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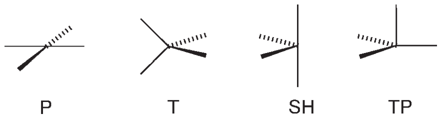
Trigonal Pyramids: Alternative Ground-State Structures for Sixteen-Electron Complexes**

Detlev Ostendorf, Clark Landis, and
Hansjörg Grützmacher*

It is widely believed that tetracoordinate complexes of d^8 transition metal centers (Rh^I, Ir^I, Pd^{II}, Pt^{II}, etc.) have a planar structure (P, ideal D_{4h} symmetry) and, indeed, hundreds of examples are known.[1] However, apart from tetrahedral structure T, which is observed for high-spin transition metals from the 4th period,[2] sawhorse (SH, C_{2v}) and trigonal-pyramidal structures (TP, C_{3v}) are alternatives (Scheme 1).[3]



Scheme 1. Planar (P), tetrahedral (T), sawhorse (SH), and trigonal-planar (TP) structures.

The highly reactive transient carbonyls $[M(CO)_4]$ (M = Fe, Ru, Os) have SH structures,[4a–c] as do a few recently isolated Ru^0 and Rh^I complexes, which show remarkable reactivity.[4d–f]

Even computationally, the TP structure has been rarely considered. Pidun and Frenking investigated by DFT methods $[RhX(CO)_3]$ complexes with X = H, HC=O, CH_2OH, and OMe. For $[Rh(HC{=}O)(CO)_3]$, TP is the (slightly) preferred ground-state structure, whereas all other complexes have either a P or an SH form in the global minimum.[5] Within the complementary spherical electron density (CSED) model, Mingos identified SH and TP forms as the next best choices to planar structures for 16-electron complexes of late transition metals.[6] In computations using the orbital ranked symmetry analysis method (ORSAM), Bayse and Hall considered d^8-MH_4 hydrides with SH and TP forms.[7] Proposals for making

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[*] Dr. D. Ostendorf, Prof. Dr. H. Grützmacher
Laboratory of Inorganic Chemistry
Department of Chemistry and Applied Biosciences
ETH Zürich
8093 Zürich (Switzerland)
Fax: (+41) 446-331-032
E-mail: gruetzmacher@inorg.chem.ethz.ch
Prof. Dr. C. Landis
Department of Chemistry
University of Wisconsin-Madison
1101 University Ave., Madison, WI 53706 (USA)
E-mail: landis@chem.wisc.edu

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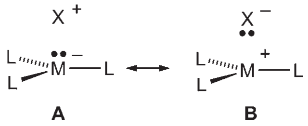
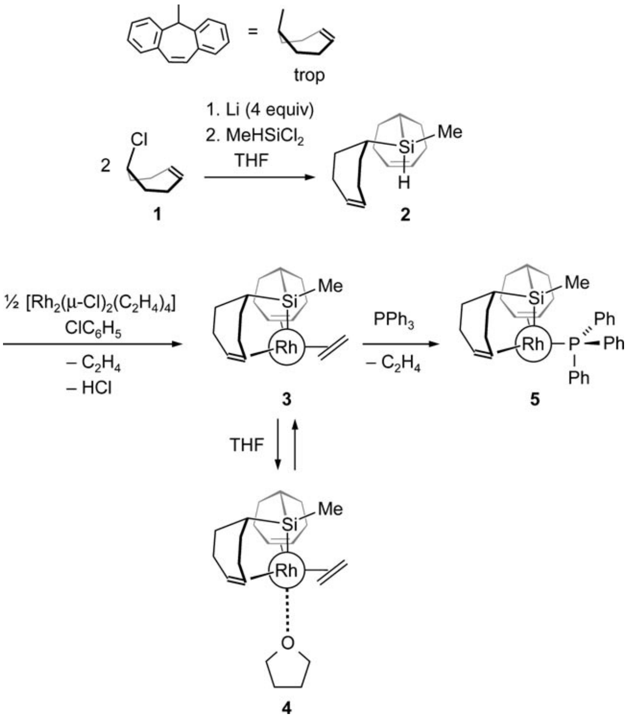
the TP forms the ground-state structures have not been made. Herein we report the synthesis and isolation of stable compounds that have such a trigonal pyramidal structure.

What ligand set would make the trigonal pyramid the ground-state structure for an ML_4 complex? We reasoned that such a structure might be obtained when the resonance form **A** contributes strongly to the electronic ground state with minimal participation of **B** (Scheme 2).



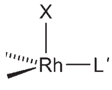
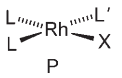
Scheme 2. Resonance structures **A** and **B** contributing to the electronic ground state of a TP structure.

This case arises when a formally d^{10}-ML_3 donor fragment such as $[Rh(C_2H_4)_3]^-$, which is known to have a trigonal-planar structure,[8] is combined with a cation X^+, most simply a proton or a silyl cation SiH_3^+. Indeed, DFT calculations for $[RhH(C_2H_4)_3]$ and $[Rh(SiH_3)(C_2H_4)_3]$ show that the trigonal-pyramidal form with H or SiH_3 in the apex is significantly more stable than the planar form (Table 1).[9]



Scheme 3. Syntheses of silane **2** and complexes **3**–**5**.

Table 1: Calculated relative energies of trigonal-pyramidal (TP) and planar (P) $[RhXL_3]$ complexes.[a]

X	L	L′	 TP E [kcal mol^{-1}]	 E [kcal mol^{-1}]
H	C_2H_4	C_2H_4	−7.3	0.0
SiH_3	C_2H_4	C_2H_4	−12.6	0.0
SiH_3	C_2H_4	PH_3	−10.6	0.0

[a] B3PW91 functional; 6-31+G* for non-metal atoms, LANL2DZ at Rh.

Remarkably, even when one π-acceptor C_2H_4 ligand is replaced by a σ-donor PH_3 ligand, the TP form of $[Rh(SiH_3)(PH_3)(C_2H_4)_2]$ is more stable (by about 11 kcal mol^{-1}) than the planar *cis*-$[Rh(SiH_3)(PH_3)(C_2H_4)_2]$ complex.[10]

None of the species in Table 1 is likely be isolated, because insertion of a coordinated C_2H_4 into the Rh–H or Rh–Si bond is expected (Rh^I complexes are efficient catalysts for hydrogenation and hydrosilylation). Therefore we synthesized bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)methylsilane ($trop_2SiHMe$, **2**), in which this insertion is unlikely to occur because of resulting strain energy in the product.[11] Silane **2** is easily obtained in 85% overall yield from 5-chloro-5*H*-dibenzo[*a*,*d*]cycloheptene (tropCl, **1**), which was first metalated with elemental lithium and then coupled in situ with $MeHSiCl_2$ (Scheme 3).

Note that the rigid conformation of **2** will not allow for a planar structure, but a sawhorse type structure may be obtainable. Silane **2** was treated with 0.5 equiv of $[Rh_2(\mu\text{-}Cl)_2(C_2H_4)_4]$ in chlorobenzene. Ethylene and HCl were liberated, and yellow crystals of $[Rh(trop_2SiMe)(C_2H_4)]\cdot C_6H_5Cl$ (**3**) precipitated in about 70% yield from the reaction mixture. When the reaction was performed in THF, or complex **3** was recrystallized from THF, $[Rh(trop_2SiMe)(C_2H_4)(thf)]$ (**4**) was obtained in 70% yield. Finally, when **3** was treated with one equivalent of PPh_3 in THF, ethylene evolved and yellow crystals of $[Rh(trop_2SiMe)(PPh_3)]$ (**5**) were isolated in almost quantitative yield.

Single crystals of **3**, **4**, and **5** were investigated by X-ray diffraction[12] (Figures 1–3). Clearly, **3** has the predicted trigonal-pyramidal structure; the calculated and experimental data agree satisfactorily (see legend to Figure 1). The three coordinated C=C units lie in the basal plane and bind in a trigonal fashion to the Rh atom, which deviates slightly (0.125 Å) from the plane through ct1–ct3 towards the inside of the pyramid (Figure 1b). The ct-Rh-Si angles are close to 90°. In the crystal lattice, one molecule of chlorobenzene lies between two molecules of **3**, but the absence of contacts shorter than 3.63 Å rules out any bonding interaction.

The structural parameters of the core of **4** are very similar to those of **3**. The Rh^I atom deviates by 0.085 Å from the plane through ct1–ct3 (Figure 2). A THF molecule binds loosely to the Rh^I center and completes the trigonal-bipyramidal coordination sphere typical of an 18-electron d^8-ML_5 complex. The very long Rh^I–O distance (2.544 Å) indicates a very weak interaction.

The crystal lattice of the phosphane silanide complex **5** contains no further solvent molecules, and the complex also has the predicted trigonal-pyramidal structure: The sum of the basal bond angles around the rhodium center is 356.6°. Like in **3** and **4**, the angles enclosed by the centroids of the coordinated C=C bonds and the apical Si atom are close to 90°. The ct-Rh-ct angle (129.6°) in **5** is somewhat wider than

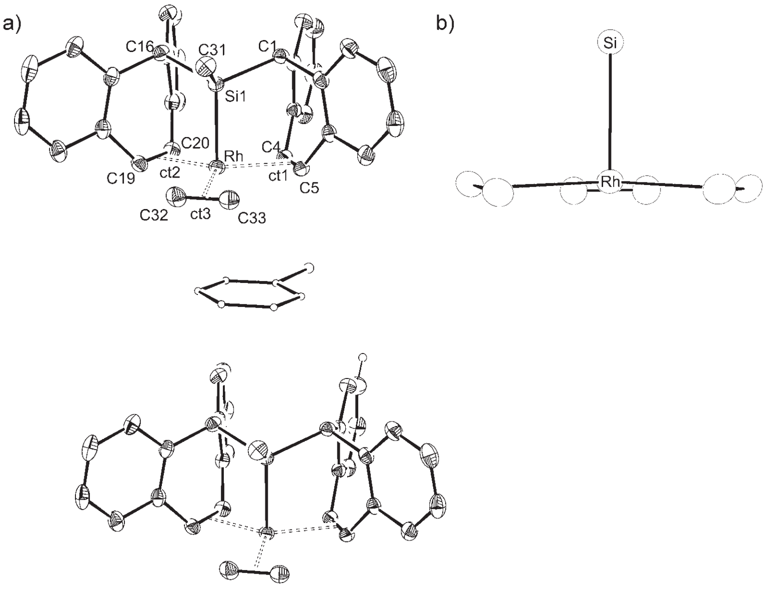


Figure 1. a) Structure of **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Bond lengths [Å] and angles [°]: Rh–Si1 2.236(1), Rh1A–Si1A 2.266(2), Rh–C4 2.203(3), Rh–C5 2.217(3), Rh–C19 2.185(3), Rh–C20 2.217(3), Rh–C32 2.222(3), Rh–C33 2.231(3), Rh–ct1 2.095(3), Rh–ct2 2.085(3), Rh–ct3 2.117(3), Si1–C16 1.910(3), Si1–C1 1.912(3), Si1–C31 1.874(3), $C4{=}C5_{trop}$ 1.405(4), $C19{=}C20_{trop}$ 1.408(4), C32=C33 1.381(4); ct1-Rh-ct2 125.2(1), ct1-Rh-ct3 115.9(1), ct2-Rh-ct3 117.9(1), ct1-Rh-Si1 91.9(1), ct2-Rh-Si1 91.8(1), ct3-Rh-Si1 96.8(1), C1-Si1-C16 112.6(1), C1-Si1-C31 106.0(1), C31-Si1-C16 105.2(1), C1-Si1-Rh 107.6(1), C16-Si1-Rh 107.9(1), C31-Si1-Rh 117.8(1). ct = centroid of the coordinated C=C bond. Σ(ct-Rh-ct) = 359.0°; Σ(C-Si-C) = 323.7°. b) Plot of the core of **3**. Computed data for $[Rh(SiH_3)(C_2H_4)_3]$: Rh–Si 2.270, Rh–ct1 2.103, Rh–ct2 2.101, Rh–ct3 2.103, Rh–C 2.214–2.217, C=C 1.397; ct-Rh-ct 119.8, Σ(H-Si-H): 320.5°; Σ(ct-Rh-ct) = 359.3°.

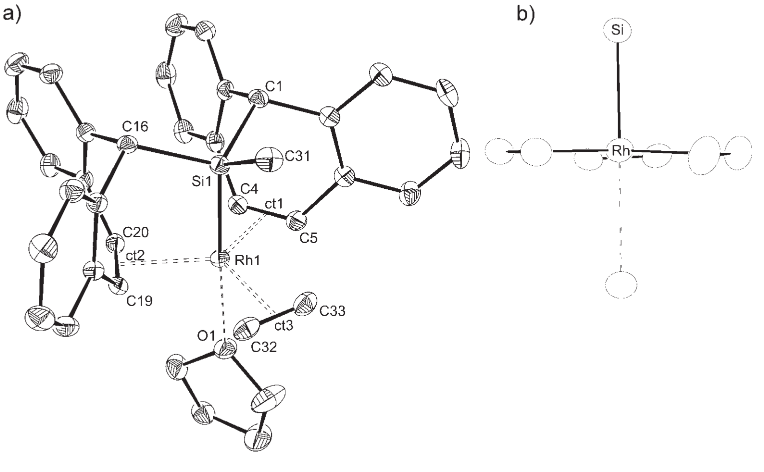


Figure 2. a) Structure of **4**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Bond lengths [Å] and angles [°]: Rh1–Si1 2.243(1), Rh1–O1 2.544(2), Rh1–C4 2.202(2), Rh1–C5 2.192(2), Rh1–C19 2.213(2), Rh1–C20 2.241(2), Rh1–C32 2.211(2), Rh1–C33 2.211(3), Rh1–ct1 2.080(2), Rh1–ct2 2.113(2), Rh1–ct3 2.102(3), Si1–C16 1.911(2), Si1–C1 1.917(2), Si1–C31 1.875(2), $C4{=}C5_{trop}$ 1.410(3), $C19{=}C20_{trop}$ 1.410(3), C32=C33 1.373(4); ct1-Rh1-ct2 122.9(1), ct1-Rh1-ct3 119.1(1), ct2-Rh1-ct3 117.5(1), ct1-Rh1-Si1 91.8(1), ct2-Rh1-Si1 91.1(1), ct3-Rh1-Si1 94.2(1), ct1-Rh1-O1 81.6(1), ct2-Rh1-O1 92.0(1), ct3-Rh1-O1 89.7(1), C1-Si1-C16 112.7(1), C1-Si1-C31 104.8(1), C31-Si1-C16 103.4(1), C1-Si1-Rh1 107.7(1), C16-Si1-Rh1 108.5(1), C31-Si1-Rh1 119.9(1). Σ(ct-Rh-ct) = 359.5°; Σ(C-Si-C) = 320.9°. b) Plot of the core of **4**.

those in **3** and **4**, while the ct-Rh-P angles are slightly more acute (111.8, 115.2°). The Rh–Si bonds in **3** (2.236(1) and 2.266(2) Å), **4** (2.243(1) Å), and **5** (2.235(1) Å) are remarkably short, even shorter than the formal Rh=Si bonds in Rh^I silylene complexes.[13a] The Rh–P distance of 2.335(1) Å lies within the upper range of Rh–P bond lengths (ca. 2.26–2.34 Å).[14]

All structural features of the core are well reflected by the computed data for the unconstrained model $[Rh(SiH_3)(PH_3)(C_2H_4)_2]$ (see legend to Figure 3). Only the experimentally determined P-Rh-Si angle in **5** (103.4(1)°) is larger than the calculated one (91.1°), certainly due to steric interactions, which can also be made responsible for the larger displacement of the Rh center from the basal plane of 0.220 Å. The acute C38-P1-Rh1 angle (94.9(1)°), which is significantly smaller that the other two C-P-Rh angles (130.4° and 118.0°), is noteworthy. This distortion may indicate a positive hyperconjugative interaction of the P–C σ bond with the empty orbital at the Rh^I center pointing outwards from the basal plane to the missing apical corner of a trigonal-bipyramidal (TBP) structure. Such distortions were also observed for complexes with SH-type structure, in which a P–C σ bond of an apically bonded PR_3 ligand may interact with an unfilled orbital pointing to the missing equatorial site of a TBP structure.[4d,e]

The NMR data of **3** and **5** are compatible with the structures observed in the solid state. In particular, the ^1H NOESY spectrum of **5** shows intense cross-peaks for the protons of the SiMe group and the phenyl protons of the PPh_3 ligand indicative of a *cis* arrangement. Such interactions are not expected for a compound in which the PPh_3 group is *trans* to the SiMe group. In the ^1H and ^{13}C NMR spectra of all reported compounds, the significant shift of the olefinic CH resonances to lower frequencies (coordination shifts $\Delta\delta_{coord} = \delta_{complex} - \delta_{ligand}$: ^1H: approx. −2 ppm, ^{13}C: approx. −60 ppm)[15] indicates significant metal-to-ligand backdonation. However, the inequivalent ^1H environments of the coordinated $H_2C{=}CH_2$ molecule in **3** lead to a slightly broadened singlet at room temperature; even at low temperature (183 K) no sharp distinct signals were observed, and this indicates a rather low barrier for rotation around the Rh–ct3 axis.

The NMR data of **3** in CD_2Cl_2 and of the THF complex **4** in $[D_8]$THF are almost identical. We therefore assume that the equilibrium **3** + THF$\rightleftharpoons$**4** lies far to left and that the interaction of the rhodium center with a fifth ligand in the apical position *trans* to the Si atom is very weak. In particular, the ^{29}Si and ^{103}Rh NMR resonances, which one would expect to respond most sensitively to complexation of an additional fifth

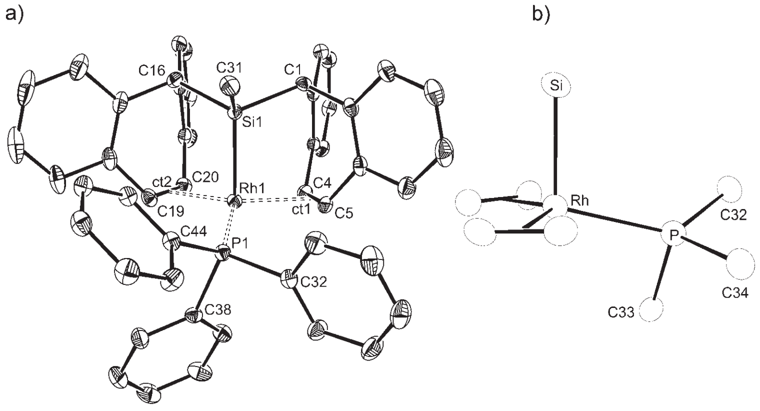


Figure 3. a) Structure of **5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Bond lengths [Å] and angles [°]: Rh1–Si1 2.235(1), Rh1–C4 2.179(3), Rh1–C5 2.211(3), Rh1–C19 2.182(3), Rh1–C20 2.157(3), Rh1–P1 2.335(1), Rh1–ct1 2.077(3), Rh1–ct2 2.048(3), Si1–C16 1.915(3), Si1–C1 1.906(3), Si1–C31 1.872(3), P1–C32 1.824(3), P1–C38 1.832(3), P1–C44 1.826(3), $C4{=}C5_{trop}$ 1.420(4), $C19{=}C20_{trop}$ 1.432(4); ct1-Rh1-ct2 129.6(1), ct1-Rh1-P1 111.8(1), ct2-Rh1-P1 115.2(1), ct1-Rh1-Si1 93.1(1), ct2-Rh1-Si1 93.0(1), P1-Rh1-Si1 103.4(1), C1-Si1-C16 112.2(1), C1-Si1-C31 103.9(1), C31-Si1-C16 106.6(1), C1-Si1-Rh1 105.9(1), C16-Si1-Rh1 106.2(1), C31-Si1-Rh1 122.2(1), Rh1-P1-C32 118.0(1), Rh1-P1-C38 94.9(1), Rh1-P1-C44 130.4(1). Σ(ct-Rh-ct) = 356.6°; Σ(C-Si-C) = 322.7°. b) Plot of the core of **5**. Computed data for $[Rh(SiH_3)(PH_3)(C_2H_4)_2]$ (C_{2v}): Rh–Si 2.279, Rh–P 2.342, Rh–ct 2.051, Rh–C 2.158–2.180, C=C 1.410; P-Rh-Si 91.1, H-P-Rh 2×121.4, H-P-Rh 119.4, ct-Rh-ct 131.0, ct-Rh-P 114.2, Σ(ct-Rh-ct) = 359.5°; Σ(H-Si-H) = 319.4°.

ligand, do not differ much (**3**: $\delta(^{29}Si) = 100.4$, $\delta(^{103}Rh) = -712.6$; **4**: $\delta(^{29}Si) = 97.15$, $\delta(^{103}Rh) = -654.5$]. Furthermore, no cross-peaks between the olefinic protons and α-CH_2 protons of the THF molecule were observed. These observations are in line with predictions made with the CSED model and the general expectations for the *trans* influence: The LUMO of a trigonal-pyramidal d^8-ML_4 complex is rather high in energy and "unavailable" for binding of a nucleophile.[6] Note, however, that planar d^8-ML_4 complexes are even more reluctant to interact with nucleophiles when a distortion from planarity is suppressed. Furthermore, trigonal-bipyramidal d^8-ML_5 complexes, conventionally obtained from planar d^8-ML_4, have the kinetically labile ligand in an equatorial position. Those obtained from TP complexes show lability in the axial position. The remarkable high-frequency shifts of the ^{29}Si NMR resonances in **3**–**5** (ca. +100 ppm vs. −10.4 ppm in **2**) would be formally in accord with a high weight of resonance structure **A** (Scheme 1) but should not be overinterpreted.

Finally, a cyclic voltammogram of **3** in THF with 0.1 M nBu_4NPF_6 showed one irreversible oxidation wave at +0.6 V and two irreversible reduction waves at −3.1 and −3.3 V versus ferrocenium/ferrocene. This demonstrates the high thermodynamic stability of the neutral molecule with a trigonal-pyramidal structure with respect to its cation and anion, respectively.

Clearly, the trigonal-pyramidal form is a possible ground state structure for d^8-ML_4 complexes. Our investigations indicate that a ligand set composed of at least one very strong (H, SiR_3) and two very weak σ-donor but good π-acceptors (olefins) favors the TP form. A deeper investigation of the electronic structure and factors that stabilize trigonal-pyramidal molecules as well as their potential use as Lewis acids with a well-defined rigid structure[16] is underway.

Experimental Section

All syntheses were performed under an atmosphere of argon by using standard Schlenk techniques. Details of the syntheses and a complete listing of spectroscopic data are given in the Supporting Information.

2: A slight excess of lithium powder (0.310 g, 44.7 mmol) was added to a solution of **1**[17] (5.00 g, 22.1 mmol) in THF (25 mL) at −78 °C. The mixture was stirred for 30 min at 0 °C and for 2 h at room temperature. The resulting deep red solution was added to a solution of dichloromethylsilane (1.26 g, 11.0 mmol) in THF (20 mL) at 0 °C. After stirring overnight, all volatile compounds were evaporated; the residue was taken up in 50 mL of toluene, the suspension filtered, and **2** was isolated from the filtrate as a pale yellow solid which was used without further purification. Yield: 4.07 g (9.5 mmol, 86 %). M.p. 58 °C. ^1H NMR (500.2 MHz, CD_2Cl_2): $\delta = -0.27$ (d, $^3J_{HH} = 3.6$ Hz, 3H; CH_3), 4.28 (m, 1H; SiH), 6.65 (d, $^3J_{HH} = 11.9$ Hz, 2H; CH_{olefin}), 6.75 ppm (d, $^3J_{HH} = 11.9$ Hz, 2H; CH_{olefin}). ^{13}C NMR (125.8 MHz, CD_2Cl_2): $\delta = -3.20$ (s, 1C; CH_3), 132.69 (s, 2C; CH_{olefin}), 133.09 ppm (s, 2C; CH_{olefin}). ^{29}Si NMR (99.4 MHz, CD_2Cl_2): $\delta = -10.44$ ppm.

3: $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ (46 mg, 0.117 mmol) and **2** (100 mg, 0.234 mmol) were dissolved in chlorobenzene (1 mL) at 0 °C. After 20 min the color of the reaction mixture had changed from bright orange to brownish yellow. Over 4 d at −20 °C pale yellow crystals of **3** formed. Yield: 109 mg (0.171 mmol, 70 %). M.p. > 124 °C (decomp.). ^1H NMR (500.2 MHz, CD_2Cl_2): $\delta = -0.93$ (s, 3H; CH_3), 4.72 (d, $^3J_{HH} = 10.5$ Hz, 2H; CH_{olefin}), 4.94 ppm (d, $^3J_{HH} = 10.5$ Hz, 2H; CH_{olefin}). ^{13}C NMR (125.8 MHz, CD_2Cl_2): $\delta = -4.78$ (s, 1C; CH_3), 70.12 (d, $^1J_{RhC} = 6.7$ Hz, 2C; CH_{olefin}), 71.00 (s, 2C; $CH_{ethylene}$), 73.92 ppm (*d*, $^1J_{RhC} = 8.2$ Hz, 2C; CH_{olefin}). ^{29}Si NMR (99.4 MHz, CD_2Cl_2): $\delta = 100.35$ ppm (d, $^1J_{RhSi} = 45.3$ Hz). ^{103}Rh NMR (15.8 MHz, CD_2Cl_2): $\delta = -712.58$ ppm (s).

4: $[Rh_2(\mu_2\text{-}Cl)_2(C_2H_4)_4]$ (46 mg, 0.117 mmol) and **2** (100 mg, 0.234 mmol) were dissolved in THF (1 mL) at room temperature. Gas evolution (C_2H_4) was observed and after 5 min the solution was concentrated to 0.5 mL, shortly warmed to about 40 °C, and cooled to room temperature. Pale yellow crystals of **4** began to precipitate, and the mixture was stored at 7 °C for 10 d. Yield: 70 % (103 mg, 0.164 mmol). M.p. > 178 °C (decomp). ^1H NMR (500.2 MHz, 263 K, $[D_8]$THF): $\delta = -1.07$ (s, 3H; CH_3), 3.02 (s, 4H; $CH_{ethylene}$), 4.68 (d, $^3J_{HH} = 10.4$ Hz, 2H; CH_{olefin}), 4.87 ppm (d, $^3J_{HH} = 10.4$ Hz; 2H, CH_{olefin}). ^{13}C NMR (125.8 MHz, 263 K, $[D_8]$THF): $\delta = -6.26$ (s, 1C; CH_3), 69.46 (d, $^1J_{RhC} = 6.7$ Hz, 2C; $CH_{2,ethylene}$), 69.49 (d, $^1J_{RhC} = 6.7$ Hz, 2C; CH_{olefin}), 72.85 ppm (d, $^1J_{RhC} = 7.9$ Hz, 2C; CH_{olefin}). ^{29}Si NMR (99.4 MHz, $[D_8]$THF): $\delta = 97.15$ (d, $^1J_{SiRh} = 45.2$ Hz). ^{103}Rh NMR (15.8 MHz, $[D_8]$THF): $\delta = -654.54$ ppm.

5: **4** (55 mg, 0.087 mmol) was treated with triphenylphosphane (23 mg, 0.088 mmol) in THF (1 mL) at room temperature. Ethylene evolution was observed and after 5 min the solution was layered with hexane (1 mL) and cooled to −15 °C. Yellow crystals of **5** were isolated by filtration and dried in vacuo (67 mg, 0.085 mmol, 97 %). M.p. > 161 °C (decomp). ^1H NMR (500.2 MHz, $[D_8]$THF): $\delta = -0.28$ (d, $^4J_{PH} = 2.8$ Hz, 3H; CH_3), 3.86 (m, 2H; CH_{olefin}), 4.29 ppm (m, 2H; CH_{olefin}). ^{13}C NMR (100.6 MHz, $[D_8]$THF): $\delta = 1.75$ (dd, $^3J_{CP} = 10.6$ Hz, $^2J_{CRh} = 1.5$ Hz, 1C; CH_3), 65.97 (dd, $^1J_{CRh} = 8.6$ Hz, $^2J_{CP} = 4.7$ Hz, 2C; CH_{olefin}), 70.74 ppm (dd, $^1J_{CRh} = 12.6$ Hz, $^2J_{CP} = 9.0$ Hz, 2C; CH_{olefin}). ^{29}Si NMR (79.5 MHz, $[D_8]$THF): $\delta = 103.68$ (dd, $^1J_{SiRh} = 47.6$ Hz, $^2J_{SiP} = 5.8$ Hz). ^{31}P NMR (161.9 MHz, $[D_8]$THF): $\delta =$

30.90 ppm (d, $^1J_{\mathrm{PRh}} = 138.6$ Hz). ^{103}Rh NMR (12.6 MHz, [D$_8$]THF): $\delta = -484.14$ ppm (d, $^1J_{\mathrm{PRh}} = 139.0$ Hz).

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Keywords: alkene ligands · density functional calculations · rhodium · Si ligands · silanes

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[1] The Cambridge Crystallographic Data Centre (CCDC) cites more than 1600 Rh$^{\mathrm{I}}$ complexes with approximately planar structures.

[2] a) For tetrahedral [Co$^{\mathrm{I}}$XL$_3$], see: S. Deblon, L. Liesum, J. Harmer, H. Schönberg, A. Schweiger, H. Grützmacher, *Chem. Eur. J.* **2002**, *8*, 601, and references therein; b) for tetrahedral Ni$^{\mathrm{II}}$ complexes, see: C. O. Dietrich-Buchecker, J. Guilhem, J.-M. Kern, C. Pascard, J.-P. Sauvage, *Inorg. Chem.* **1994**, *33*, 3498, and references therein.

[3] We refer to trigonal pyramids as structures in which the angles between the axial and equatorial ligands are equal or close to 90°. Alternatively, they may be described as trigonal bipyramids in which one axial coordination site is vacant. A referee brought to our attention that MS$_3$(L) fragments (M = V, Mo, Fe) with TP structures were observed in transition metal sulfide clusters: a) I. Noda, B. S. Snyder, R. H. Holm, *Inorg. Chem.* **1986**, *25*, 3851; b) E. Nordlander, S. C. Lee, W. C. Cen, Z. Y. Wu, C. R. Natoli, A. Di Cicco, A. Filipponi, B. Hedman, K. O. Hodgson, R. H. Holm, *J. Am. Chem. Soc.* **1993**, *115*, 5549.

[4] a) M. Poliakoff, J. J. Turner, *J. Chem. Soc. Dalton Trans.* **1974**, 2276; b) M = Ru: P. L. Bogdan, E. Weitz, *J. Am. Chem. Soc.* **1989**, *111*, 3163; c) calculations: J. Li, G. Schreckenbach, T. Ziegler, *J. Am. Chem. Soc.* **1995**, *117*, 486. For a general discussion, see: T. A. Albright, J. K. Burdett, M.-H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, **1985**, pp. 360, 404; d) P. Maire, A. Sreekanth, T. Büttner, J. Harmer, I. Gromov, H. Rüegger, F. Breher, A. Schweiger, H. Grützmacher, *Angew. Chem.* **2006**, *118*, 3343; *Angew. Chem. Int. Ed.* **2006**, *45*, 3265; e) P. Maire, T. Büttner, F. Breher, P. Le Floch, H. Grützmacher, *Angew. Chem.* **2005**, *117*, 6477; *Angew. Chem. Int. Ed.* **2005**, *44*, 6318; f) M. Ogasawara, D. Huang, W. E. Streib, J. C. Huffman, N. Gallego-Planas, F. Maseras, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1997**, *119*, 8642, and references therein.

[5] U. Pidun, G. Frenking, *Chem. Eur. J.* **1998**, *4*, 522.

[6] D. M. P. Mingos, *J. Organomet. Chem.* **2004**, *689*, 4420.

[7] C. A. Bayse, M. B. Hall, *J. Am. Chem. Soc.* **1999**, *121*, 1348.

[8] [Ag(C$_2$H$_4$)$_3$]$^+$: I. Krossing, A. Reisinger, *Angew. Chem.* **2003**, *115*, 5903; *Angew. Chem. Int. Ed.* **2003**, *42*, 5725.

[9] All DFT calculations were carried out with the Gaussian 03 set of programs and the B3PW91 functional (for details see Supporting Information). For [Rh(SiH$_3$)(C$_2$H$_4$)$_3$], the isomer with the SiH$_3$ group in the basal plane is less stable by 14 kcal mol^{-1} and corresponds more to an alkyl complex [Rh(CH$_2$CH$_2$SiH$_3$)(C$_2$H$_4$)$_2$], that is, one ethylene ligand has inserted into the Rh–Si bond. For [Rh(SiH$_3$)(PH$_3$)(C$_2$H$_4$)$_2$] no energy minimum for an isomer with a basal SiH$_3$ group was found.

[10] The isomer with the SiH$_3$ and PH$_3$ groups in *trans* positions adopts a SH-type structure which is almost equal in energy to the planar *cis* form ($\Delta E = -0.03$ kcal mol^{-1}).

[11] The synthesis of the related dibenzophosphasemibullvalene was recently reported: J. Geier, G. Frison, H. Grützmacher, *Angew. Chem.* **2003**, *115*, 4085; *Angew. Chem. Int. Ed.* **2003**, *42*, 3955.

[12] Pale yellow, air-sensitive single crystals of **3** were obtained from chlorobenzene solution at −15 °C. Crystal data: C$_{39}$H$_{34}$ClRhSi; monoclinic; space group $P2(1)/c$; $a = 10.6913(5)$, $b = 11.5133(6)$, $c = 24.6594(12)$ Å; $V = 3020.2(3)$ Å^3; $Z = 4$; $\rho_{\mathrm{calcd}} = 1.437$ Mg m^{-3}; crystal dimensions $0.36 \times 0.20 \times 0.11$ mm; Bruker SMART Apex diffractometer with CCD area detector; Mo$_{\mathrm{K\alpha}}$ radiation ($\lambda = 0.71073$ Å), 200 K, $2\Theta_{\max} = 56.56°$; 30672 reflections, 7483 independent ($R_{\mathrm{int}} = 0.0249$); direct methods; empirical absorption correction with SADABS (version 2.03); refinement against full matrix (versus F^2) with SHELXTL (version 6.12) and SHELXL-97 (G. M. Sheldrick, Göttingen, 1997); 291 parameters, $R1 = 0.0390$ and $wR2$ (all data) = 0.1107, max./min. residual electron density 0.908/−0.473 e Å^{-3}. All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms in their calculated positions was included in the refinement by using a riding model. The chlorobenzene units and the units of **3** show an alternating alignment. Furthermore, four percent of the molecules of **3** are disordered about a mirror plane perpendicular to the Rh–Si1 bond (Rh1A–Si1A). The remaining atoms of the disordered molecules overlap with the ligand atoms of the main structure and could therefore not be localized. Pale yellow, air-sensitive single crystals of **4** were obtained from a solution in THF at room temperature. Crystal data: C$_{37}$H$_{37}$OSiRh; orthorhombic; space group $P2(1)2(1)2(1)$; $a = 10.9270(5)$, $b = 12.2839(6)$, $c = 21.6322(10)$ Å; $V = 2903.6(2)$ Å^3; $Z = 4$; $\rho_{\mathrm{calcd}} = 1.438$ Mg m^{-3}; crystal dimensions $0.24 \times 0.19 \times 0.15$ mm; Bruker SMART Apex diffractometer with CCD area detector; Mo$_{\mathrm{K\alpha}}$ radiation ($\lambda = 0.71073$ Å), 200 K, $2\Theta_{\max} = 56.62°$; 30385 reflections, 7220 independent ($R_{\mathrm{int}} = 0.0388$); direct methods; refinement against full matrix (versus F^2) with SHELXTL (version 6.12) and SHELXL-97; 362 parameters, $R1 = 0.0280$ and $wR2$ (all data) = 0.0626, max./min. residual electron density 0.930/−0.378 e Å^{-3}. All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms in their calculated positions was included in the refinement by using a riding model. Yellow, air-sensitive single plates of **5** were obtained from a solution in THF layered with *n*-hexane at 7 °C. Crystal data: C$_{49}$H$_{40}$SiPRh; monoclinic; space group $P2(1)/c$; $a = 17.0615(8)$, $b = 10.3224(5)$, $c = 22.1621(11)$ Å; $V = 3778.5(3)$ Å^3; $Z = 4$; $\rho_{\mathrm{calcd}} = 1.390$ Mg m^{-3}; crystal dimensions $0.30 \times 0.22 \times 0.06$ mm; Bruker SMART K1 diffractometer with CCD area detector; Mo$_{\mathrm{K\alpha}}$ radiation ($\lambda = 0.71073$ Å), 200 K, $2\Theta_{\max} = 52.75°$; 30210 reflections, 7723 independent ($R_{\mathrm{int}} = 0.0447$); direct methods; empirical absorption correction with SADABS (version 2.03); refinement against full matrix (versus F^2) with SHELXTL (version 6.12) and SHELXL-97; 476 parameters, $R1 = 0.0327$ and $wR2$ (all data) = 0.0799, max./min. residual electron density 0.754/−0.463 e Å^{-3}. All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms in their calculated positions was included in the refinement by using a riding model. CCDC-602113 (**3**), -602114 (**4**), and -602115 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] To date, 71 compounds with an Rh–Si bond are listed in the CCDC data base. For recent examples with Rh$^{\mathrm{I}}$–Si bonds, see: a) E. Neumann, A. Pfaltz, *Organometallics* **2005**, *24*, 2008; b) R. Goikhman, M. Aizenberg, Y. Ben-David, L. J. W. Shimon, D. Milstein, *Organometallics* **2002**, *21*, 5060; c) M. Okazaki, S. Ohshitanai, H. Tobita, H. Ogino, *J. Chem. Soc. Dalton Trans.* **2002**, 2061.

[14] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, *J. Chem. Soc. Perkin Trans. 2* **1987**, S1.

[15] See for comparison: P. Maire, F. Breher, H. Schönberg, H. Grützmacher, *Organometallics* **2005**, *24*, 3207.

[16] Note that most Lewis acids change their structure on complexation of a nucleophile, for instance, from trigonal planar to tetrahedral.

[17] G. Berti, *J. Org. Chem.* **1957**, *22*, 230.